Chemical Properties of Corn Pericarp as a Renewable Resource(Digest_要約)

AUTHOR(S):

Yoshida, Tomoki

Abstract of Doctor Thesis

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Author: Tomoki Yoshida

Chapter 1: General introduction

Importance of corn as a source of materials for food, feed, starch industry, production of functional oligosaccharides etc. was described with introduction of common classification into 6 types in relation to the quality of accumulated starch and appearance of kernels. Then, importance of corn pericarp (CP) as a renewable resource was also strengthened, because a huge amount of CP is annually produced from corn starch industry as a by-product. In this chapter, the objective of this thesis is described directed to develop innovative methods for effective use of CP as a renewable source of polysaccharides. For achievement of this objective, microwave-assisted extraction method and a kind of cellulose solvent comprising NaOH and urea were explained for application to extract polysaccharides present in CP. Furthermore, the importance of characterization of water sorption behavior and film forming ability of arabinoxylan, which is the major hemicellulosic polysaccharides in CP, was explained for quality control of corn kernels as well as practical use of its components. In addition, the author mentioned about development of a new technique of affinity chromatography on cellulose, which makes it possible to purify β-glucan in one-step. Finally, a constitution of the whole chapters in this thesis was noted.

Chapter 2: Microwave-assisted extraction of carbohydrates from corn pericarp

Carbohydrates were effectively extracted from CP by microwave-assisted extraction (MAE). The optimum condition for MAE of carbohydrates was determined by using response surface methodology with experiment design including fractional factorial design, the path of steepest ascent and central composite design. Carbohydrate yield attained 70.8% of total carbohydrate content in CP at the optimum condition [heating temperature 176.5°C, come-up time 2 min, heating time 16 min and solid to liquid ratio 1/20 (g/mL)]. Additionally, the optimum condition was desirable for predominant production of xylo-oligosaccharides. In this chapter, the author clearly demonstrated applicability of MAE as an effective tool for use of CP as a carbohydrates resource.

Chapter 3: Development of a new mild method for extraction of hemicellulosic polysaccharides including arabinoxylan from corn pericarp

Extractability of hemicellulosic polysaccharides including arabinoxylan and β-glucan by using NaOH-urea solvent system from CP was described in this chapter. Solubilization rate of CP by the present system attained 72.2% at the condition of 2% NaOH-6M urea. The extracted hemicelluloses could form transparent films whose mechanical properties were 56.2 MPa, 3.5% and 3.09 GPa for breaking stress (σ_{max}), maximum strain (ε_{max}) and elastic modulus (E), respectively, as evaluated by tensile tests. These values were 1.2-, 1.3- and 0.94-fold higher than those obtained for the film of arabinoxylan alone. These results suggested that the developed system is an attractive technique desirable not only for convenient extraction of hemicelluloses from CP but also for the utilization of the extracted materials as a source of flexible biofilms.

Furthermore, similarity of the over-all chemical compositions observed among the CPs isolated from the 6 types of matured corn kernels. The exception was only observed in the β-(1,3;1,4)-glucan content (3.2%) of CP from sweet corn.

Chapter 4: Water sorption property of corn pericarp arabinoxylan

In this chapter, the role of arabinose substituents of arabinoxylan for its water sorption properties was discussed. Preparation of the CP arabinoxylan with removal of arabinose substituents was firstly carried out by partial acid hydrolysis at pH 1.0 for 1-6 h at 37-57°C. The extent of removal was followed by regression analysis with the method of least squares. Using the regression profile, three kinds of desubstituted arabinoxylans having arabinose/xylose (A/X) ratios of 0.25, 0.12 and 0.03 with mean molecular weights of 37.3×10^3, 15.6×10^3 and 7.2×10^3, respectively, was prepared from native arabinoxylan (A/X ratio of 0.35 and mean molecular weight of 53.6×10^3). All CP arabinoxylans were in the amorphous state and the film forming ability of the native state was lost after partial acid hydrolysis. The decrement in the degree of arabinose substitution decreased its solubility.

All arabinoxylan samples gave similar sigmoid shaped adsorption isotherms grouped in IUPAC type II. When isotherms were analyzed on the basis of the independent dual sorption model and the Hailwood-Horrobin model, the former model was found to be preferable for demonstrating that removal of arabinose pendants from the main (1,4)-linked xylan chain gradually reduces the Langmuir capacity of the CP arabinoxylan. Results provided crucial information expected for industrial utilization of arabinoxylan and indicated the application potentiality of the independent dual sorption model to characterize hydration behavior of the other kind of branched polymers.

Chapter 5: Extraction of β-(1,3;1,4)-glucan from corn pericarp

In this chapter, the condition of the NaOH-urea solvent system was optimized for extraction of β-(1,3;1,4)-glucan (β-glucan) present in CP with investigation of effects of cellulose crystallinity on extractability of β-glucan. Three repetitions of the freeze (-20°C)-thaw treatment allowed extraction of almost all β-glucan (97.8%) present in CP. Disruption of cellulose crystalline property was prerequisite for extraction of β-glucan fraction amounting approximately 20% which was firmly interacted with cellulose. Availability of this technique to extract β-glucan from oat meal and barley flour in high rates also was shown, 82.8% for the former and 92.5% for the latter. The present NaOH-urea solvent system with repetition of the freeze-thaw treatments may be a new extraction technique for extraction of β-glucan from various cereal materials.

Chapter 6: Isolation and properties of corn pericarp β-(1,3;1,4)-glucan

In the chapters 3 and 5, the author demonstrated the effectiveness of a NaOH-urea solvent system for extraction of hemicellulosic polysaccharides including arabinoxylan and β-glucan from CP. In this chapter, effectiveness of the combination of anion-exchange and cellulose affinity chromatographic techniques was established for the first time to isolate β-glucan by separation of large amount of coexisting arabinoxylan. By using the present system, purity of the β-glucan was increased from 6.6% to 84.7%. The methylation and fragmentation analyses showed that the isolated β-glucan has the ratios of (1,4)/(1,3) linkage and cellotriosyl/cellotetraosyl segments of 2.60 and 2.5, respectively. The chemical structure of the β-glucan was also confirmed by ^{13}C-NMR spectroscopic analysis.

Conclusions

In conclusion, the present thesis showed important characteristics of polysaccharides in CP and provided the new applications and techniques for use of CP as a biomass resource, allowing more effective utilization of corn kernels not only for food and feed, but also for preparation of valuable polysaccharide-based innovative materials in the future.